Designing High Li-Ion Transference Number and High Stable Electrolytes for Lithium Batteries

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Lawrence Berkeley National Laboratory
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Project ID: bat419

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Overview

Timeline

- Start Date: Oct. 1, 2015
- End Date: Sept. 2019

Barriers Addressed

- Energy Density
- Safety
- Low rate capability

Budget

- Total budget (4 years): $1,075K
- FY19 funding: $250K

Partners/Collaborators

Kristin Persson (UCB/LBNL), for molecular dynamics studies
Vince Battaglia (LBNL), for preparation of porous anodes and cathodes
Nitash Balsara (UCB/LBNL), for electrochemical characterization of transport properties

Relevance

- **Sluggish ion transport** through the electrolyte phase of porous electrodes **limits utilization (capacity), particularly a**t **high rates**, of thick electrodes needed for high energy density EV batteries.
- High Li-ion transference number electrolytes have been theorized to reduce these transport limitations, thereby enabling higher energy density and higher rate capabilities in Li-ion batteries
- High Li transference number electrolytes have also been theorized to suppress dendrite growth during lithium metal stripping and plating, which could provide a route to enable safe, stable Li electrodes

Objectives for FY19

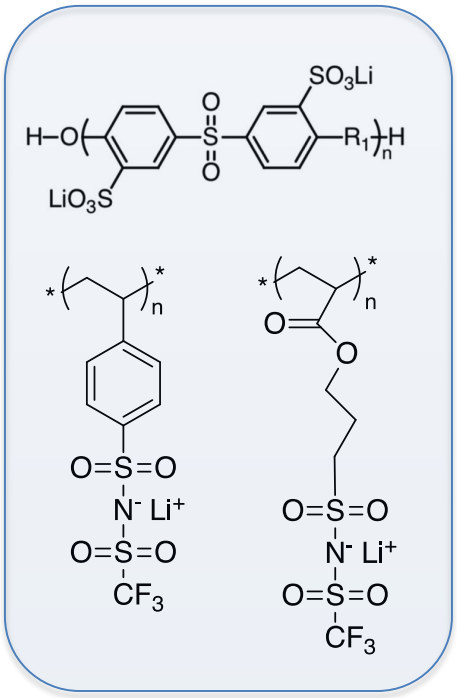
- Overall project goal: develop polyelectrolyte solutions (charged polymers in liquid solvents) as high conductivity and transference number electrolytes for Li-ion and Li metal batteries.
- Understand how ion transport is influenced by the following polyelectrolyte solution properties: polymer composition, solvent properties, additives, added binary salt, and appended ion chemistry.
- Use this knowledge to design, and then implement in a Li-ion battery, polyelectrolyte solutions with optimal transport and stability properties.

Milestones

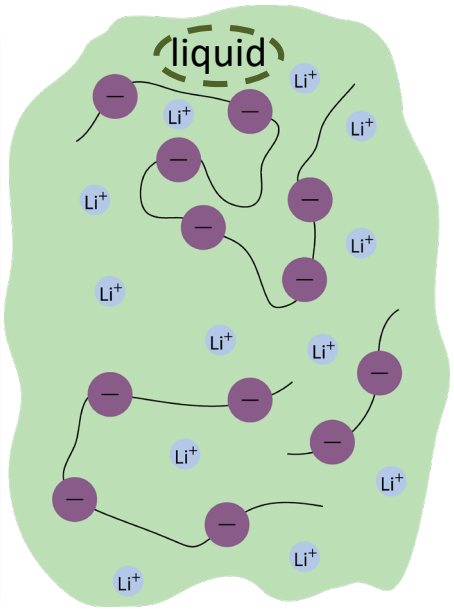
Date	Milestones	Status
December 2018	Complete synthesis and characterization of a new Li^+-neutralized charged polymer (PSTFSI) with a triflimide-like ion appended to the polymer backbone to improve ion dissociation.	Completed
March 2019	Complete NMR transport and viscosity measurements of PSTFSI dissolved in carbonate-based solvents.	Completed
June 2019	Complete electrochemical transport measurements of PSTFSI in symmetric cells with Li metal electrodes and stainless steel electrodes.	On track
September 2019	Complete characterization of rate capabilities of cells comprised of Li metal, a porous NMC cathode, and PSTFSI containing carbonate solutions during electrochemical cycling.	On track

Approach

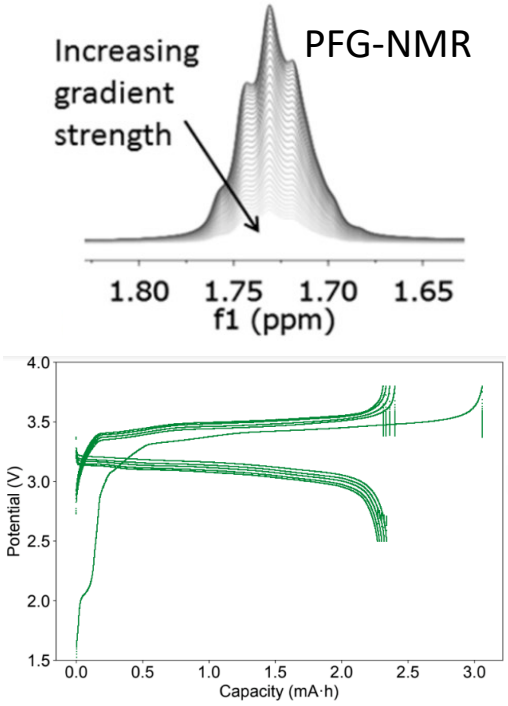
- Synthesize single ion-conducting polymers that have high solubility in battery-relevant solvents.
- Prepare polyelectrolyte solutions to study influence of additives, binary salt addition, solvent composition, and polymer choice.
- Characterize transport properties using a combination of AC impedance, pulsed field gradient NMR (self-diffusion coefficients), viscosity.
- Use ab-initio molecular dynamics to understand molecular underpinnings of ion transport trends.



Synthesis

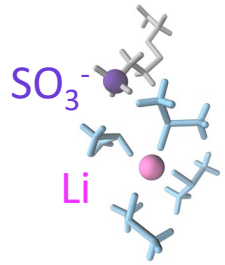


Preparation

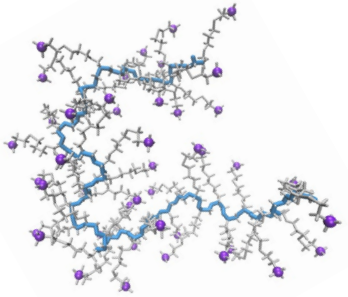


Characterization

Solvent-Separated Ion Pair (SSIP)



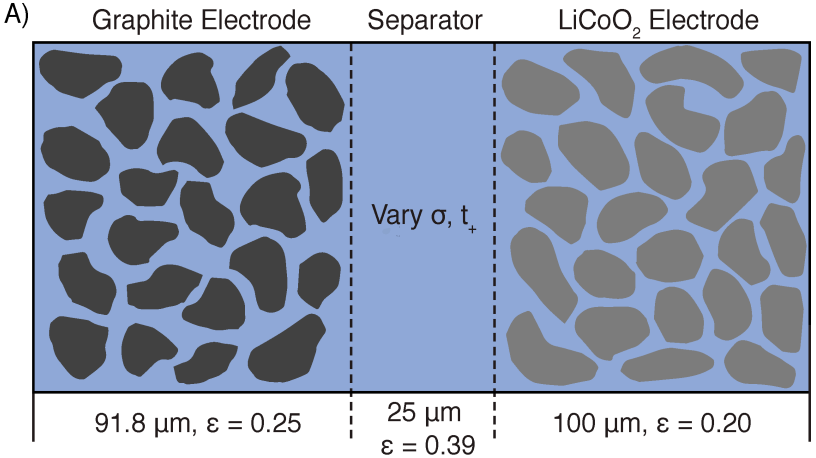
Conformation in solution



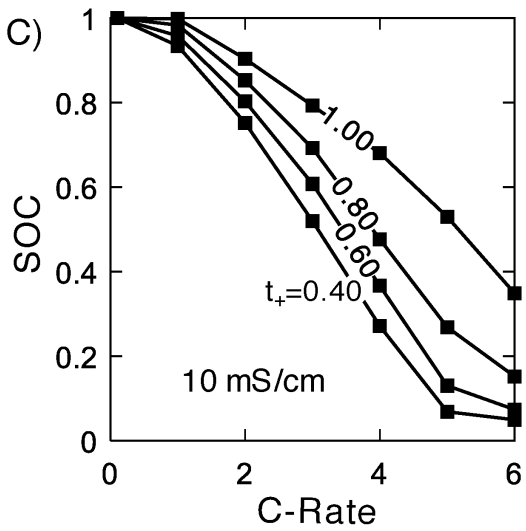
Modeling (w/ K. Persson)

Motivation to study polyelectrolyte solutions

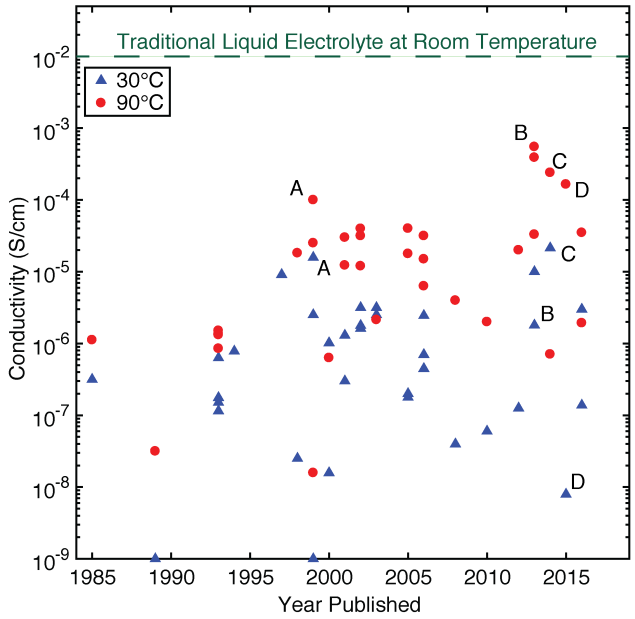
- Newman-type modeling predicts high transference number electrolytes would enable higher C-rates in Li-ion batteries

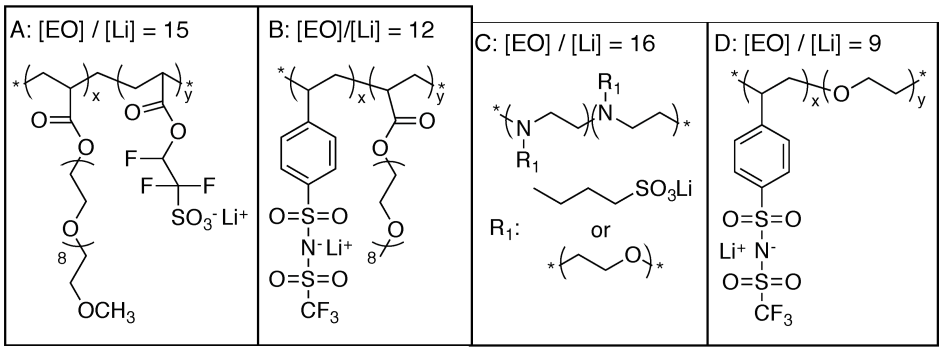


$$t_+ = \frac{D_+}{D_+ + D_-}$$



- Dry polymer electrolytes suffer from low conductivity (each point is a unique polymer)



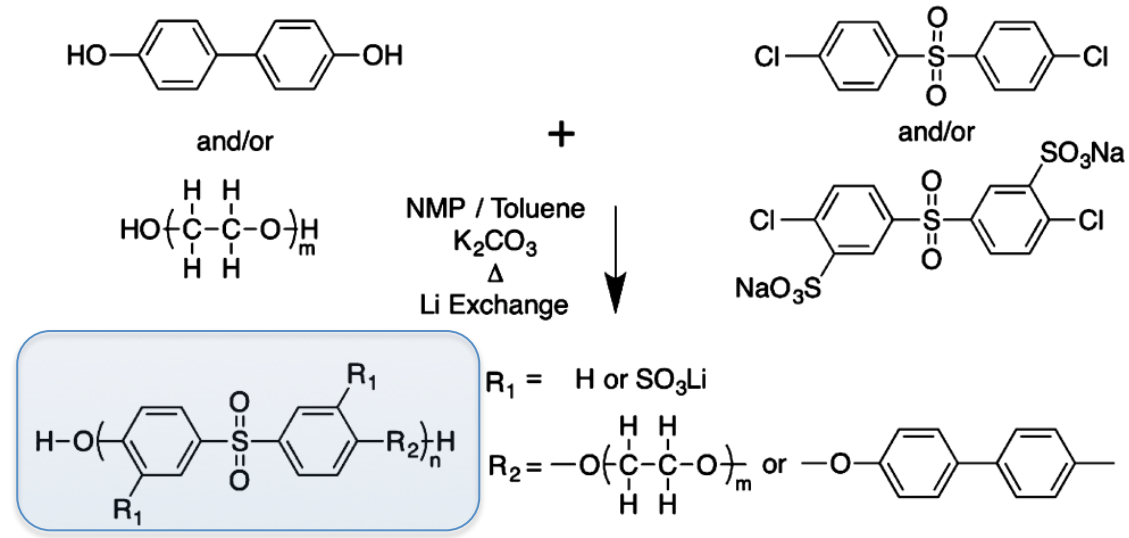


Systematically understand enhancements in transport by adding solvent

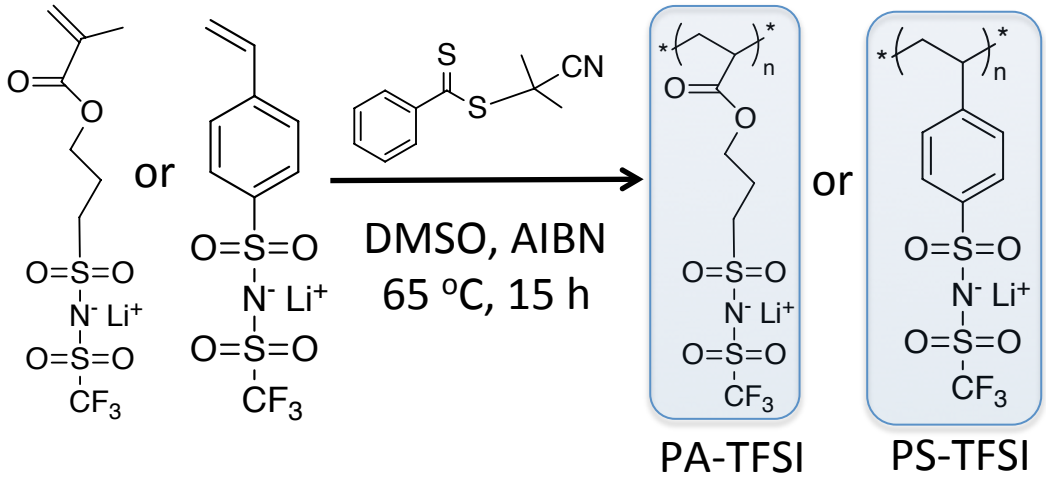
Diederichsen; McShane; McCloskey. *ACS Energy Lett.* 2017, *2*, 2563–2575.

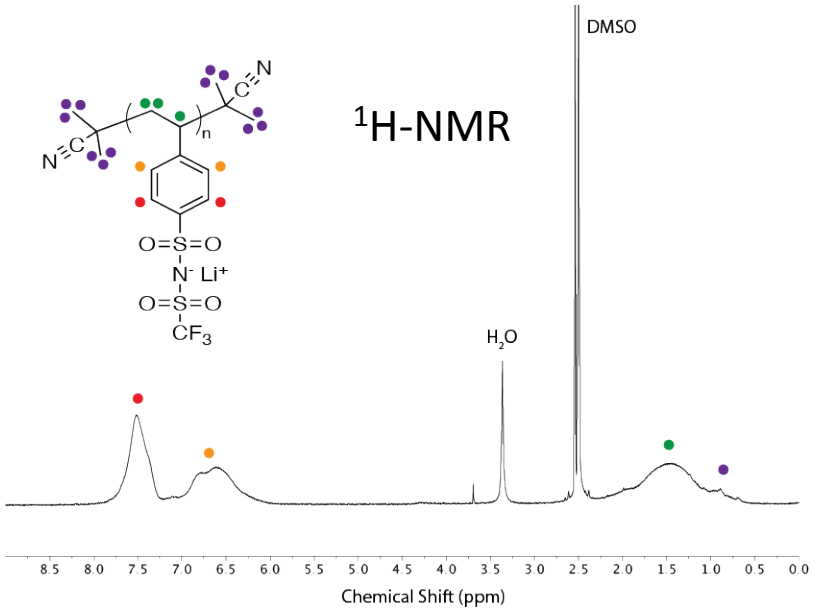
Accomplishment: synthesis of soluble ionomers

- Synthesized three ionomers, with acronyms sPSF-co-PEO, PA-TFSI, and PS-TFSI, all of which are abundantly soluble in liquid carbonates. Polymers were fully characterized to ensure purity and molecular weight.

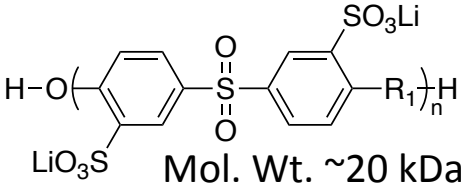


sPSF-co-PEO (from FY16)

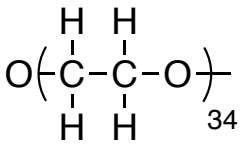


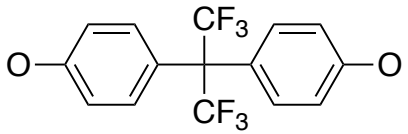


Accomplishment: Understanding solvent and added salt influence on conductivity and transference number

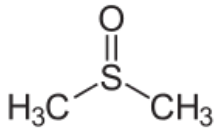


Mol. Wt. ~20 kDa

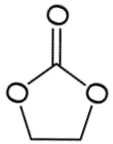
R_1= 

or 

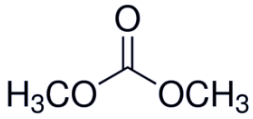
(10 mol%)



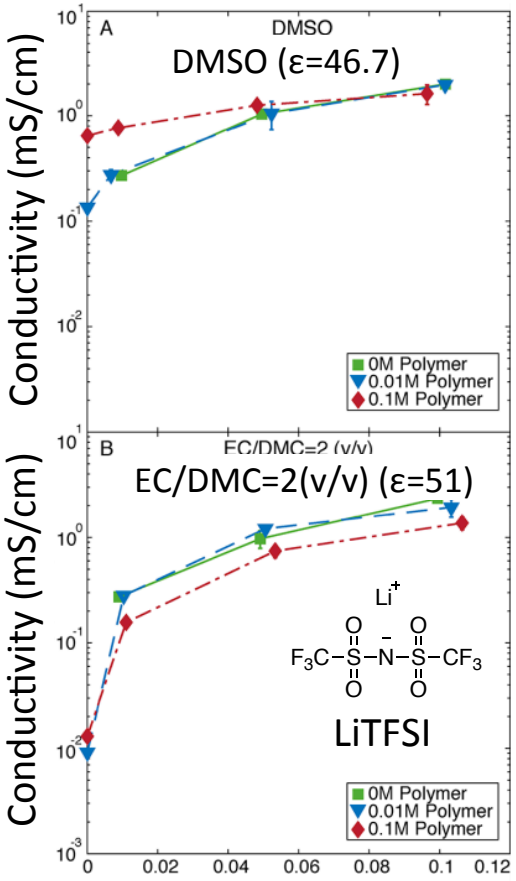
Dimethyl sulfoxide (DMSO)

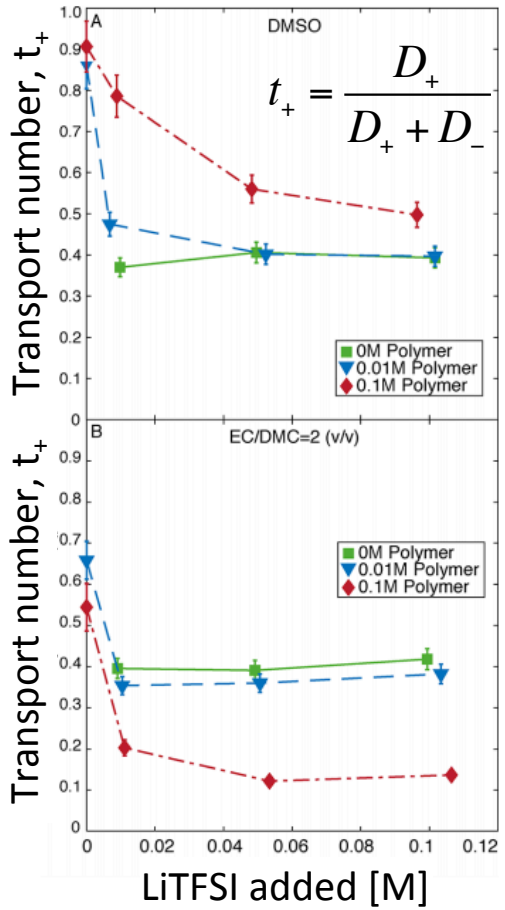


Ethylene carbonate (EC)



Dimethyl carbonate (DMC)

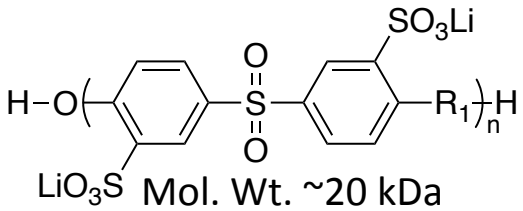




D_i measured using PFG-NMR

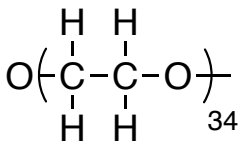
With no added salt, DMSO polyelectrolyte solutions have much higher conductivity, t_+. With added salt, conductivity is roughly equivalent, but t_+ is still higher in DMSO

Accomplishment: Understanding solvent influence on dissociation

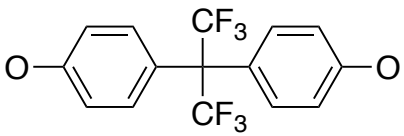


Mol. Wt. ~20 kDa

R_1=

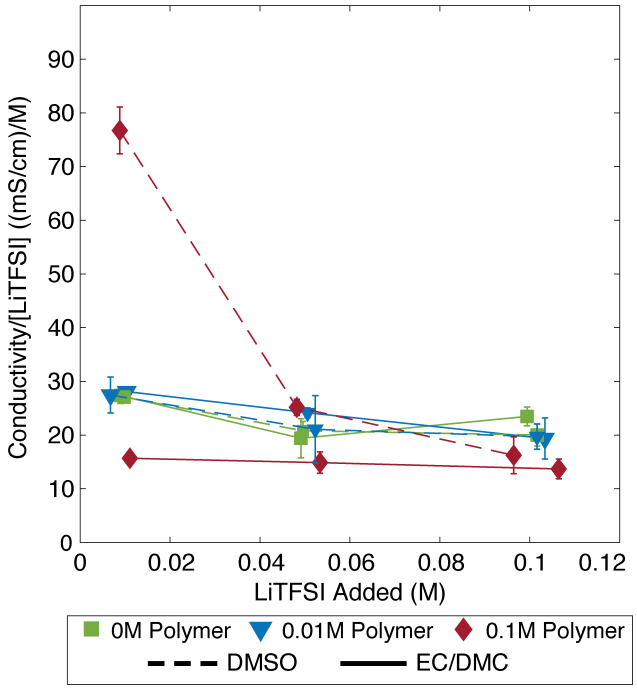


or



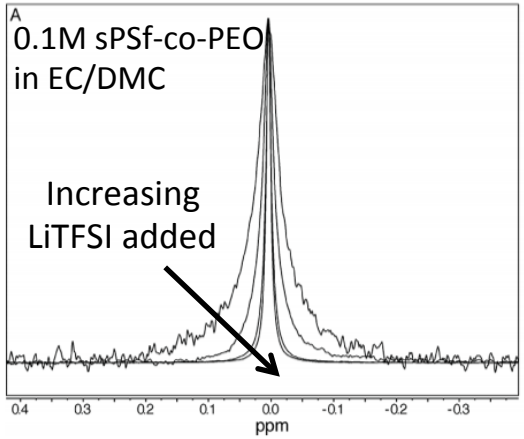
(10 mol%)

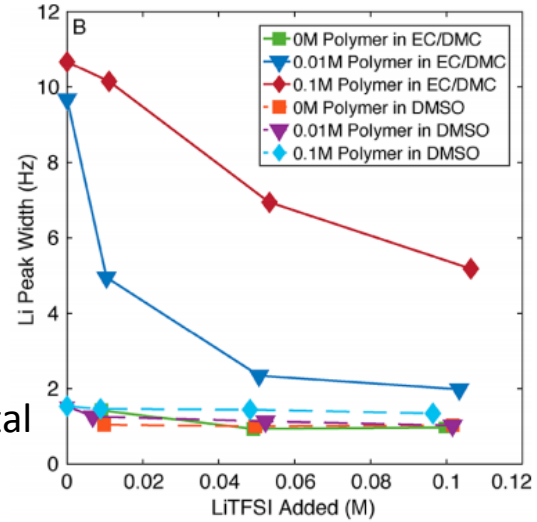
Conductivity normalized to LiTFSI concentration

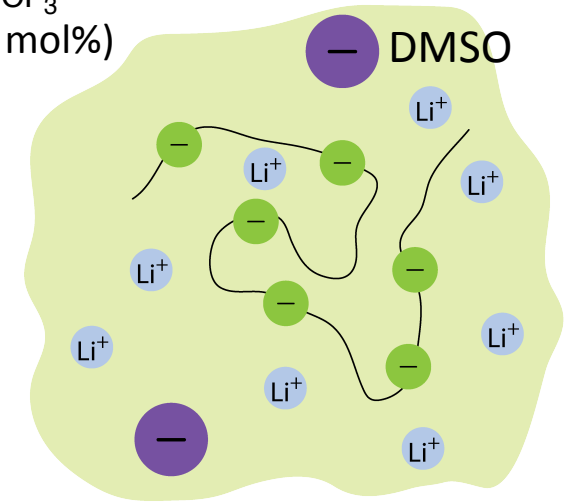


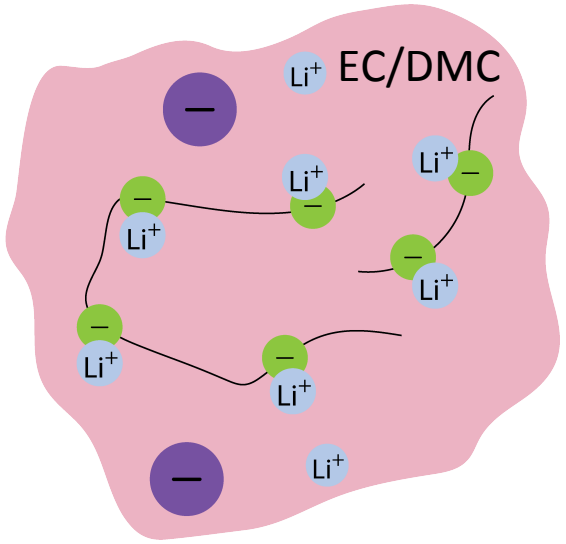
*polymer 'concentration' refers to total sulfonate concentration in solution

^{7}Li NMR peak width



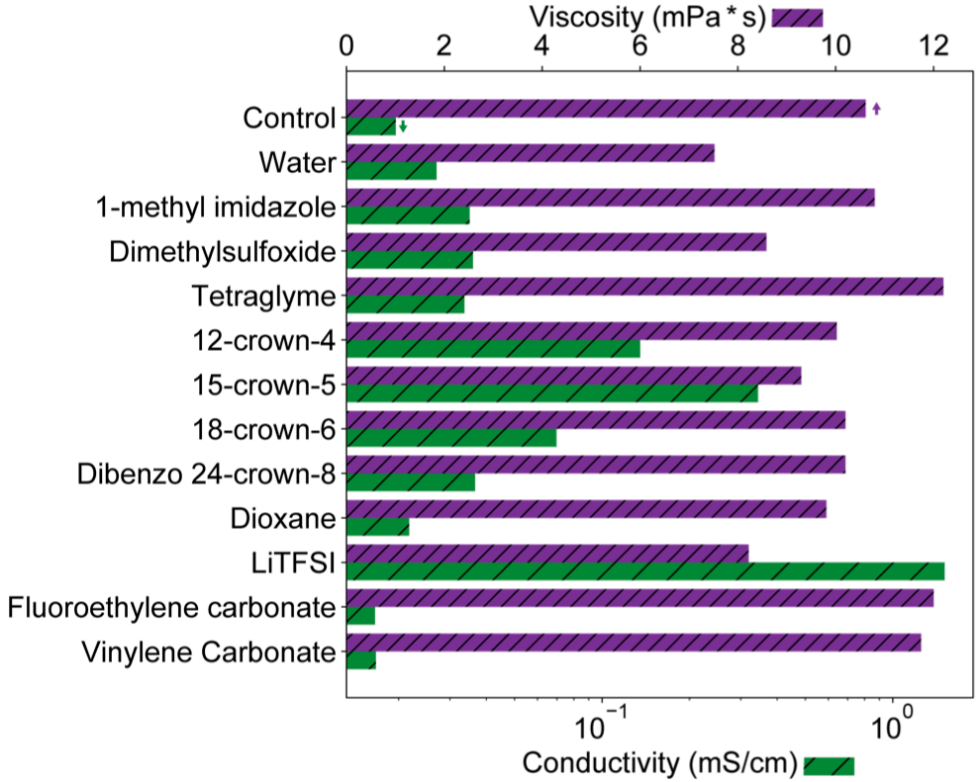


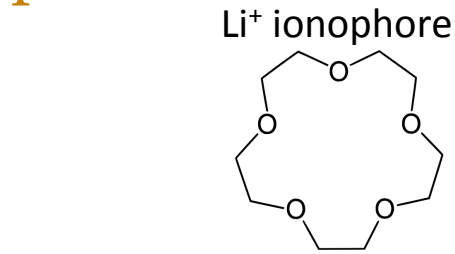


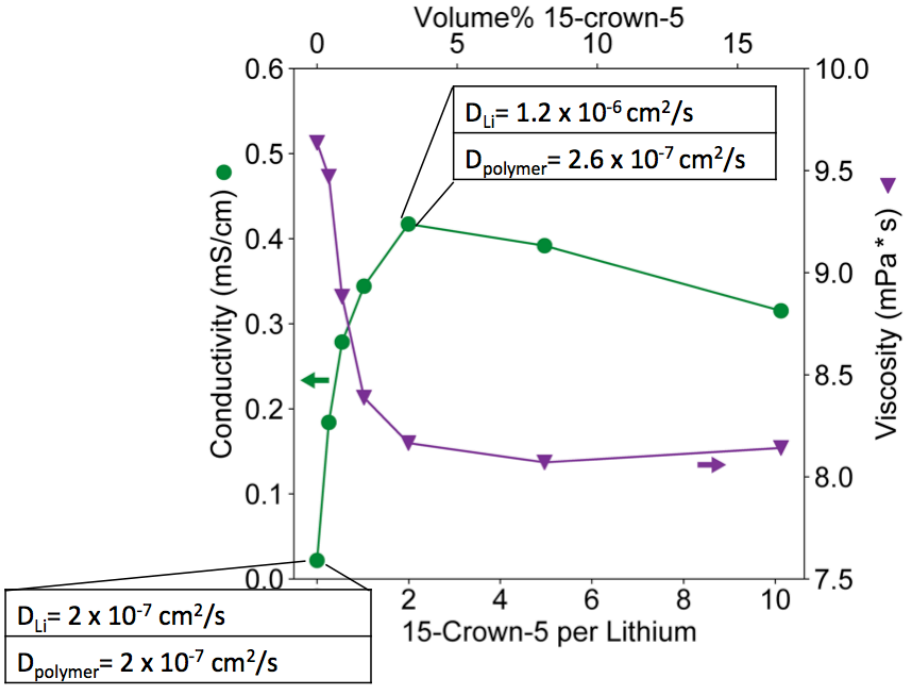


DMSO dissociates $-SO_3^-$ Li^+ in sPSF-co-PEO, whereas EC:DMC does not. Surprising given their similar dielectric constants.

Accomplishment: Additive engineering to promote conductivity



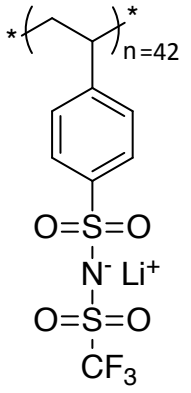




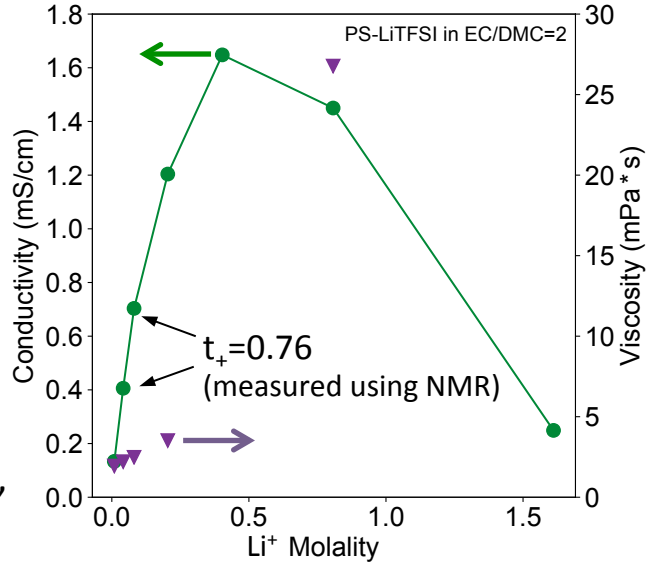
0.1M sPSF-co-PEO + 0.1M Additive in EC/DMC

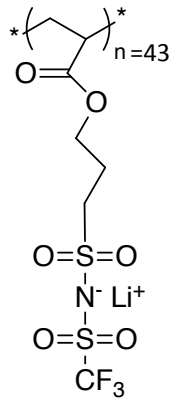
Crown ethers, specifically 15-c-5, can be used to enhance dissociation, conductivity, transference number in PSF-co-PEO in EC:DMC polyelectrolyte solutions

Accomplishment: Development of ionomers that dissociate in battery-relevant solvents (PA-TFSI, PS-TFSI)

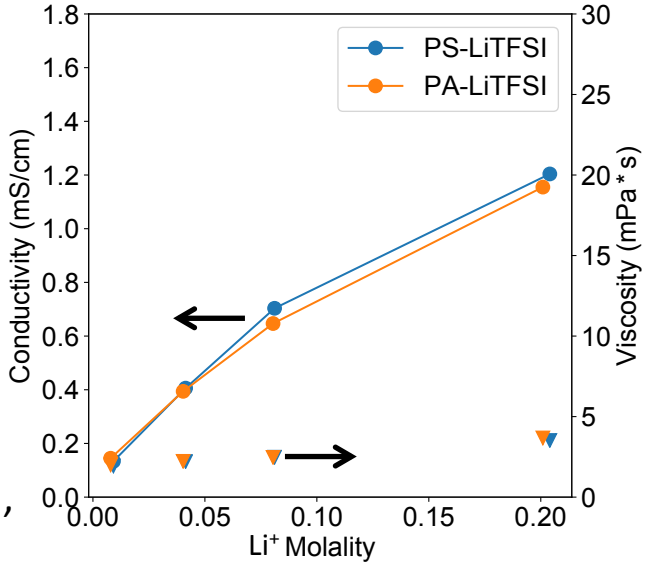


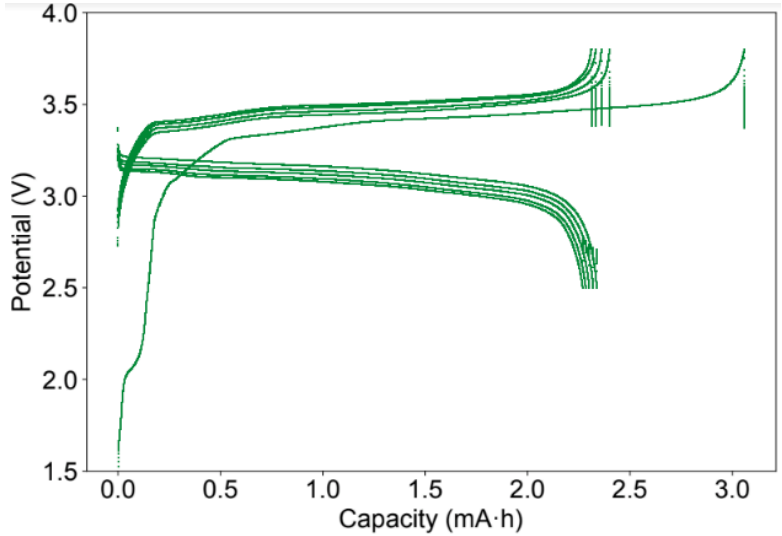
PS-TFSI
(M_n= 13.7 kDa, PD=1.28)





PA-TFSI
(M^n= 14.4 kDa, PD=1.15)





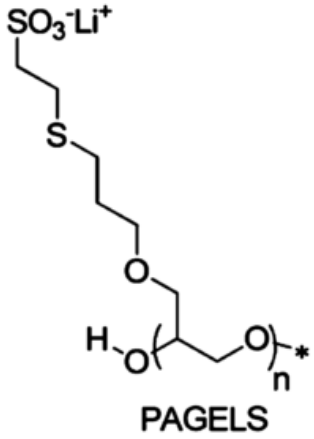
- $LiFePO_4$ cathode (70 µm thick, 30% porosity, 1.8 cm^2, 2.6 mAh)
- graphite anode
- 0.4 M Li^+ PS-TFSI in EC/DMC=2
- C/20, first 5 cycles shown

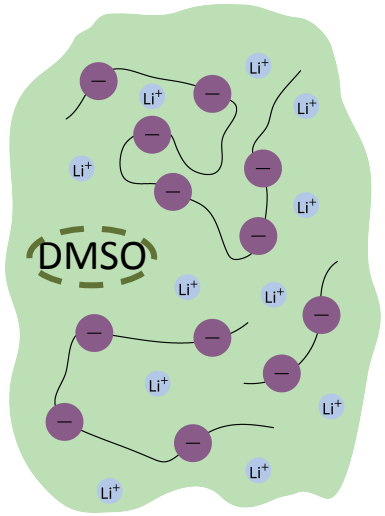
PS-TFSI and PA-TFSI provide substantial conductivity improvements over sPSF-co-PEO in battery relevant solvents. Battery testing is underway, as are refinements in composition to improve conductivity, transference number, and stability.

M_n= number average molecular weight
PD= polydispersity

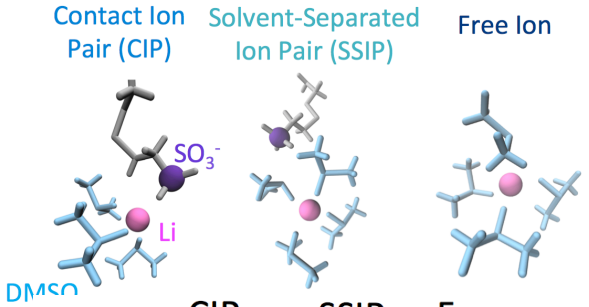
Accomplishment: understanding ion pairing in polyelectrolyte solutions through simulation

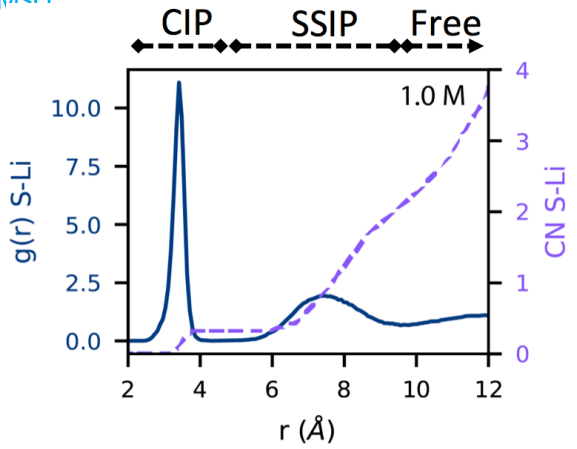
Modeled polyelectrolyte from earlier studies (FY16) using all-atom molecular dynamics simulations





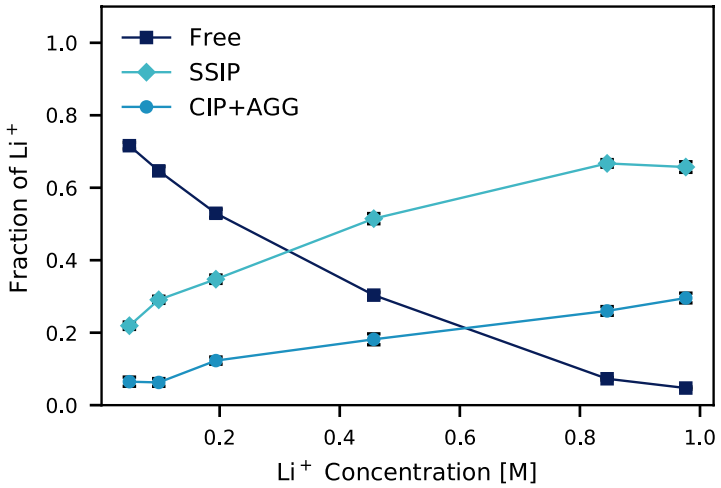
Buss, McCloskey et al. *ACS Energy Lett.* **2017**, *2* (2), 481–487





Simulation setup:

- Poly(allyl glycidyl ether)-lithium sulfonate (PAGELS)
- Single polymer chain (n=43), 43 Li^+, DMSO
- OPLS force field
- 50 ns production runs

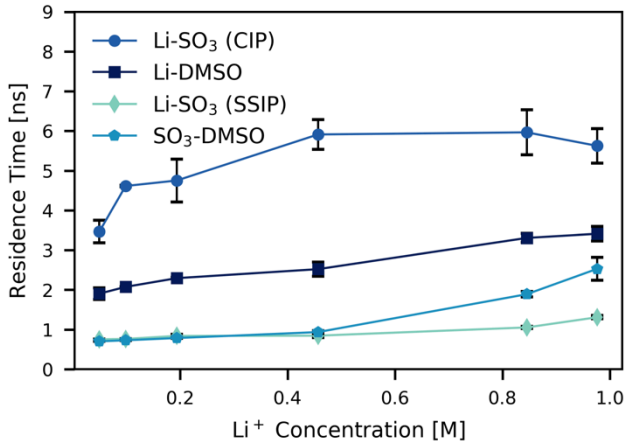


Ion pairing increases with concentration

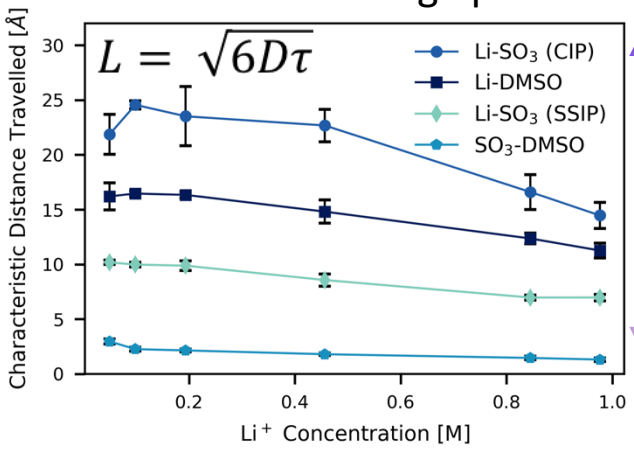
Collaboration with Kristin Persson (LBNL)

Accomplishment: understanding molecular modes of transport in polyelectrolyte solutions through simulation

Time that each pair typically spends associated with each other before 'breaking apart'

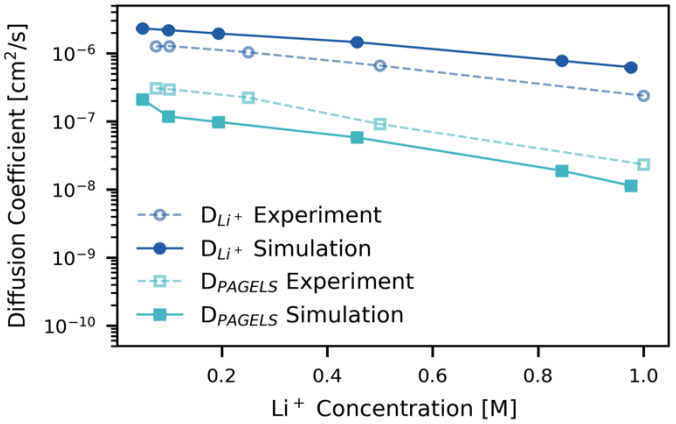


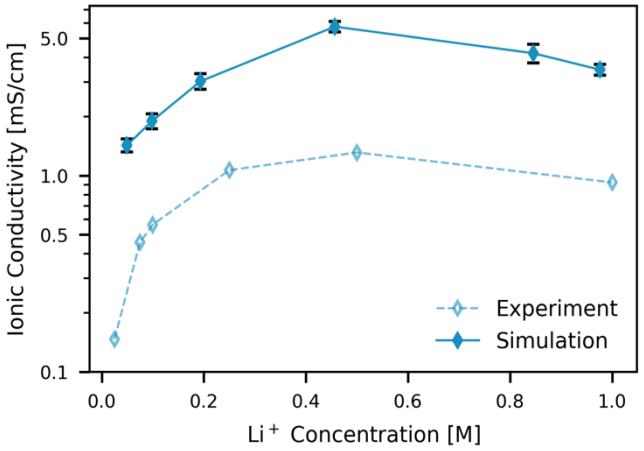
Distance each pair travels together before 'breaking apart'



More vehicular (associative) transport

More structure (hopping) diffusion





Molecular dynamics simulations satisfactorily reproduce experimental transport properties, provide insight into optimization of transport properties

Remaining challenges and barriers

- We need to continue to develop our understanding of how to optimize conductivity, transference number, and stability of polyelectrolyte solutions
  - PS-TFSI and PA-TFSI appear to be excellent model materials, but polymer (molecular weight and potentially co-monomers?), solvent, and additive (including small molecule salts) compositions to provide optimal properties are still unclear. Simulations will help elucidate these design parameters.
- Measurement of liquid electrolyte transport properties (diffusion coefficients, activity coefficients, transference number) in an operating electrochemical cell (e.g., a Li-Li symmetric cell) is non-trivial. Working with Nitash Balsara to develop these techniques for polyelectrolyte solutions.
- High voltage stability of PS-TFSI and PA-TFSI need to be characterized using NMC electrodes. Our lab is well-suited to do so.
- Li metal stability using PS-TFSI and PA-TFSI polyelectrolytes needs to established.

Proposed future research

- Further understand how to optimize polyelectrolyte solution properties to enable a safe, high energy and rate capability battery
  - Investigate the effect of solvent composition on ion transport in PS-TFSI and PA-TFSI polymer solutions, particularly to understand how to lower viscosity at high polymer concentrations
  - Investigate known additives, including small molecule salts, to enhance desirable Li metal and high voltage cathode interfacial properties, as well as to optimize conductivity in PS-TFSI and PA-TFSI solutions
  - Characterize transport properties of new electrolyte compositions using NMR diffusometry and (under-development) electrochemical methods
  - Use molecular dynamics as a tool to understand underlying molecular phenomena that control ion transport. Use this understanding to guide polymer and solution design.
  - Characterize performance of batteries (Li-ion and Li metal) that contain polyelectrolyte solutions.

Any proposed future work is subject to change based on funding levels

Summary

- Polyelectrolyte solutions provide a promising route towards liquid-like conductivities and single-ion conducting dry polymer transference numbers.
- We synthesized and fully characterized the structure of three ionomers that were fully soluble in battery-relevant solvents
- We demonstrated polyelectrolyte solutions comprised of EC/DMC as a solvent with room temperature conductivities approaching 2 mS/cm and NMR-measured transference numbers >0.8
- We identified potential additives to further enhance ion dissociation, which results in reduced viscosity and improved conductivities
- We used molecular dynamics to elucidate transport mechanisms in a previously-developed polyelectrolyte solution and plan to use MD to study our current polyelectrolyte systems
- The performance of batteries that use polyelectrolyte solutions is underway, and will encompass the development of thick porous NMC electrodes and Li metal

Publications and presentations (FY18-19)

Publications

- Diederichsen, K. M.; Fong, K.; Persson, K. A.; *McCloskey, B. D.* "Invesitgation of solvent type and salt addition in high transference number nonaqueous polyelectrolyte solutions for lithium-ion batteries." ***Macromolecules*** (2018) 51(21), 8761-8771.
- Diederichsen, K. M.; McShane, E.; *McCloskey, B. D.* "Promising routes to high lithium ion transference number electrolytes for Li batteries." ***ACS Energy Letters*** (2017) 2, 2563-2575.

Presentations

- Don Paul's 50th Anniversary Symposium, University of Texas, Austin, Oct. 2017 ***(invited presentation***). "Designing polymer-based electrolytes with high lithium ion transference number and conductivity."
- American Institute of Chemical Engineers National Meeting, Membrane Tutorial Session, Minneapolis, MN, Oct. 2017. "Transport Processes in Batteries: A Synergistic Research Direction for Membrane Scientists."
- American Institute of Chemical Engineers National Meeting, Polymers for Energy Storage and Conversion Session, Minneapolis, MN, Nov. 2017. "Breaking the Compensation Effect within the Vogel-Tammann-Fulcher Equation for Polymer-Based Electrolytes," Kyle Diederichsen presenting.
- American Chemical Society Fall Meeting, Symposium on Designing Polymers for Electrochemical Applications, Boston, MA (***invited presentation***), Aug. 2018. "Ion transport in ionomers and polyelectrolyte solutions for lithium batteries."
- Gordon Research Conference, Polymer Physics, Mount Holyoke College, MA (***invited presentation***), July 2018. "Designing polymer-based electrolytes with high lithium ion transference number and conductivity."
- Gordon Research Conference, Polymer Physics, Mount Holyoke College, MA (***poster presentation***), July 2018. "Investigation of Solvent Type and Salt Addition in High Transference Number Nonaqueous Polyelectrolyte Solutions." Kyle Diederichsen presenting.
- AIChE Annual Meeting, October 30, 2018. "Investigation of Solvent Composition and Salt Addition in High Transference Number Nonaqueous Polyelectrolyte Solutions," Kyle Diederichsen presenting.
- AIChE Annual Meeting, November 1, 2018. "Modeling of High Transference Number Electrolytes for Fast Charging Lithium Ion Batteries," Eric McShane presenting.

Critical assumptions and issues

- Past attempts at designing high transference numbers have not succeeded due to poor conductivity of resultant single-ion conductors and a poor understanding of the underlying molecular mechanisms for ion transport.
  - We aim to understand the influence of polymer/solution properties on ion transport to enable polyelectrolyte solutions with ion transport properties that are better than traditional liquid electrolytes.
  - This project is structured to develop this knowledge through a combined theory-experiment approach.
- Can we find a polymer/solution combination that is stable to both Li metal and high voltage cathodes?
  - We will leverage prior reported knowledge on useful additives to engineer beneficial interfacial properties at both electrodes.
- We assume that the 1D Newman-type model used to identify the benefits of high transference number electrolytes is not overly simplistic (e.g., it sufficiently captures the influence of solid electrolyte interface formation on electrode kinetics and transport).
  - This project will be structured to experimentally verify the importance of various electrolyte transport properties, such as the transference number, on porous electrode and battery performance.